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Electrophoretic deposition of carbon nanotube-reinforced hydroxyapatite bioactive layers on Ti–6Al–4V alloys for biomedical applications

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Abstract

Ultra-fine (20 nm) hydroxyapatite powders-reinforced with multi-walled carbon nanotubes were coated on Ti–6Al–4V medical alloy using electrophoretic deposition in an attempt to increase poor mechanical properties of hydroxyapatite, in particular inter-laminar shear strength between coating layer and implant surface. It is shown that the addition of carbon nanotubes increases both hardness, elastic modulus and inter-laminar shear strength of monolithic hydroxyapatite layers. A deposit thickness of 25 μm is also found to be critical for preventing crack formation during sintering.

Keywords: Hydroxyapatite; Carbon nanotube; Deposition

1. Introduction

Although some metallic alloys including stainless steel and Co–Cr–Mo alloy can be used for biomedical applications, such as devices for fracture fixation and external splints, Ti–6Al–4V alloys are the most common materials used for prosthesis hip replacements due to their excellent mechanical properties and low density [1]. However, after the replacement, the implant surfaces have to be accepted by the body and also a strong bond between the implants and the bone is required. Therefore, metallic implants are coated with bioactive materials, such as hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] (HA) or bioactive glass for encouraging the in-growth of natural bone into the prosthetic device using some coating technologies, such as plasma spraying (PS) [2]. Recently it has been found that when using PS for HA, due to very high temperature required by the coating process as well as rapid cooling rate, HA undergoes changes in phase composition and also crystallinity [3]. Process temperature also affects some mechanical and surface properties of the metallic implant and this causes more complications in the human body in the long term. Furthermore, when plasma spraying is used to coat the metallic implants with bioactive ceramics, the thickness of the coating layer, adherence, roughness and the microstructure of the surface are difficult to control. It is also known that when HA is used as a coating material, phase separation takes place during plasma coating due to the very high temperature required for the process and some undesirable phases (such as CaO) which are not compatible with the human body may form [4]. Furthermore, calcium oxide (CaO) has no biocompatibility and dissolves significantly faster than the other phases in physiological solution, therefore it is a detrimental phase for the overall implant structure. Moreover, as the coating surface is directly in contact with the bone and body fluid once implanted, the structure, phase composition, dissolution rate as well as the roughness of the HA layers are the critical parameters to be controlled for both fixation period and the fixation strength between the coating and bone. The second critical issue in implants coating is the mechanical bonding strength between the coating layers and metallic substrate as cracking and peeling of the coating layers are the most common problems experienced in industry and yet to be solved. Recently, some of the published papers outlined successful results on EPD-formed carbon nanotube coating layers [9,10] and it was considered in the present work that further application of the EPD technique in the formation of bioactive layers from mixed suspensions can be explored to improve mechanical properties.

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Therefore, a cost effective and low temperature coating technique that can control the necessary properties and solve the problems outlined above is used in this work in an attempt to produce HA layers reinforced with carbon nanotubes (CNTs) using electrophoretic deposition (EPD) [6–8]. It is also aimed to lower the sintering temperature of HA coating layers to 500–600 °C so that phase separation does not take place. CNTs are mixed with nano-size HA to increase the mechanical bonding of the deposited layer.

2. Experimental work

Nano-size hydroxyapatite powders used in the present work was synthesised using sol–gel technique and the details were presented elsewhere [5]. After the filtration process, HA powders with an average particle size of 20 nm were selected and mixed with commercially available multi-walled CNTs (Shenzhen Nanotech Port Co. Ltd., China) with an average tube diameter of 20 nm. HA powders were first dispersed in aqueous suspensions using Darvan C as a dispersant and the pH was adjusted to be 4. In a separate process, the surfaces of CNTc were modified using $HNO_3 + H_2SO_4$ mixture to give them a negative surface charge due to presence of COOH groups. During surface modification of CNTs, they were kept in acid mixture for 30 min and then washed twice to remove excess acid. Surface modified CNTc were then added to suspension containing dispersed HA powders and ultrasonically mixed for 3 h. Three different suspensions containing 0.5, 1 and 2 wt.% CNTs of the total powders were prepared for coating experiments. A constant suspension solids loading of 5 wt.% was used for all experiments. EPD experiments were conducted under constant voltage conditions (20 V dc) for different deposition times. Stainless steel electrodes with a separation distance of 20 mm were used for all coating experiments. The sintered (at 600 °C for 2 h under flowing nitrogen gas) samples were polished and gold coated for SEM observations. For TEM investigations, powders were placed on a cupper grid with a diameter of 3 mm and analysed under bright-field conditions. Nano-indentation tests were conducted using appropriate calibration procedure before each test and test weights. A total of six measurements were taken for each value and the minimum and maximum values were ignored and the average of remaining four values was reported.

3. Results and discussion

Transmission electron microscopy (TEM) image of the sol–gel synthesised HA powders after filtration process is shown in Fig. 1a indicating that majority of the particles have spherical shape with an average particle size of 20 nm as confirmed by the particle size measurements as well. After filtration separation, well-defined particles with absence of particle agglomeration are also evident from the image shown in Fig. 1a. FEG SEM image of CNTs used along with HA powders is shown in Fig. 1b which clearly indicates the size of the diameter to be 20 nm and homogeneous distribution of as received form. The most critical step is the homogeneous distribution of the species when two different components are

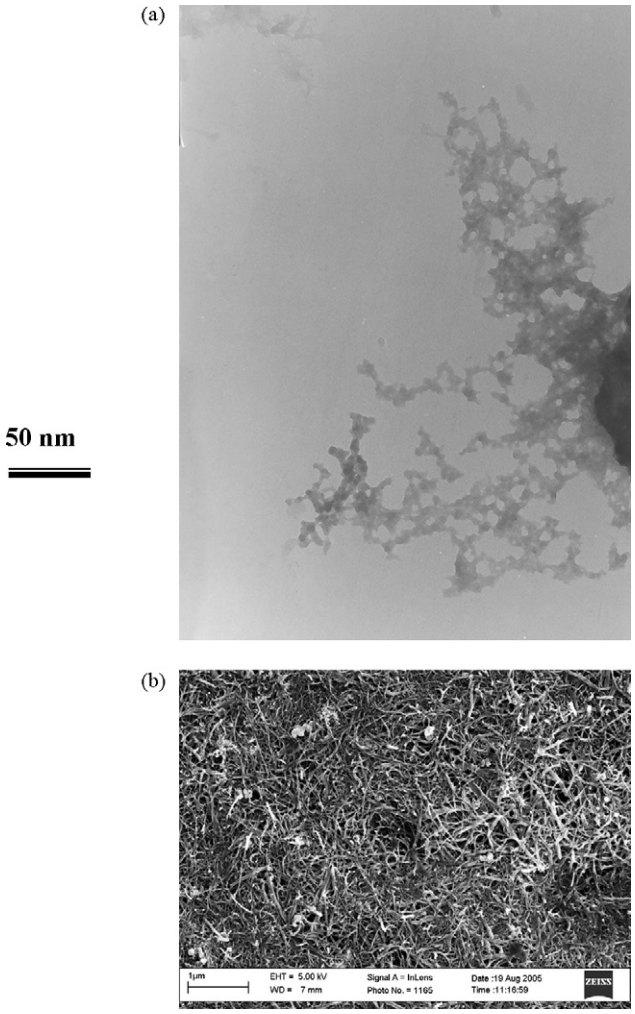

Fig. 1. TEM image of sol–gel synthesised HA powders with an average particle size of 20 nm after filtration (a) and FEG SEM image of as received CNTs (b).

mixed together (HA plus CNTs in this case) in a suspension to prevent preferential coagulation of the particles due to their surface charge. If a suspension that contains coagulated particles is used for coating experiments using EPD, deposit layers contain inhomogeneous particles and this will result in formation of surface cracks during sintering due to different shrinkage behaviour of different species within the coating layer. Therefore, in the present work the surface charge of HA and CNTs is adjusted to be opposite so that they can attract each other and act as a single composite particle during EPD under the application of an applied voltage. Detail observations of the HA plus CNTs suspensions were conducted using TEM and FEG SEM to assess the presence of stable and homogeneous structure in colloidal state. The TEM image of HA plus CNTs mixture is shown in Fig. 2a indicating that most of the CNTs are actually covered by very fine HA powders (note that all HA particles were already filtered using a nano-filter with mesh size of 20 nm therefore all HA particles used in the experiments were finer than 20 nm and some of them were about 5 nm). FEG SEM image of the mixed suspension is also indicated that due to electrostatic attraction between positively charged HA powder (as they were dispersed within the aqueous suspension

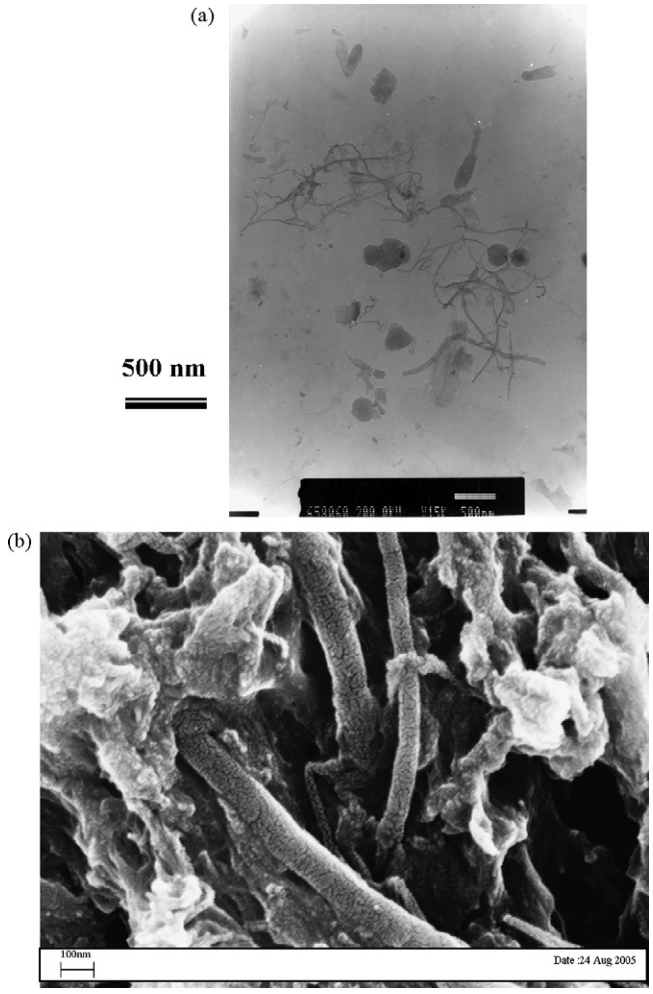

Fig. 2. TEM image of sol–gel synthesised HA powders mixed with CNTs (a) and FEG SEM image of the mixed HA plus CNTs indicating that each individual carbon nanotube is covered by the very fine HA powders (b).

at a pH value of 4) and negatively charged CNTs (due to surface modification with acids), the resultant mixture contains well-dispersed structure where CNTs are almost fully covered by the finest HA particles, as shown in Fig. 2b.

Optical microscopy image of HA and HA plus CNTs coated Ti–6Al–4V wire after sintering at 600 °C for 2 h under flowing nitrogen gas is shown in Fig. 3. The EPD-formed coating layers shown in Fig. 3 were obtained using suspensions with a constant solids loading of 5 wt.% (in the HA plus CNTs suspension, the weight ratio between HA and CNTs was kept to be 99/1), applied voltage of 20 V dc for a deposition time of 4 min. Under these parameters, homogeneous and surface crack free HA and HA plus CNTs coating layers with a deposit thickness of 25 μm were achieved as shown in Fig. 3. In a separate experiment, by keeping all other parameters fixed, but only deposition time was increased to 10 min, in an attempt to see its effect on the structure and quality of the HA plus CNTs deposit layer. Increasing the deposition time provided a deposit thickness of 40 μm and also formed extensive surface microcracks after sintering at 600 °C for 2 h as shown in Fig. 4. It is evident from Fig. 4 that the sintering process led to the generation of numerous surface microcarcks within the

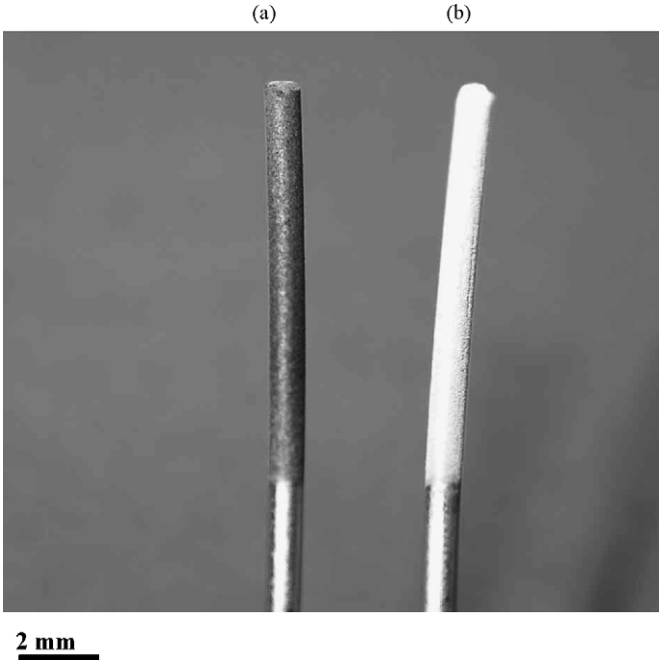

Fig. 3. Optical microscopy images of EPD-formed HA plus CNTs (a) and HA (b) coating layers on Ti–6Al–4V alloy using a deposition voltage of 20 V dc and deposition time of 4 min after sintering at 600 °C for 2 h under flowing nitrogen gas. Both suspensions contain 5 wt.% solids loading and concentration of CNTs within the second coating mixture was 1 wt.% of the total powder.

coating layer although no peeling was observed. It was contributed from Fig. 4 that the presence of CNTs within the coating layer act as reinforcement fibres to hold the coating structure together and also provided a good adhesion to the Ti–6Al–4V alloy as no peeling was observed after bending the coating substrate. However, as the coating thickness almost doubled (from 25 to 40 μm), the effect of thermal expansion between Ti alloy and HA plus CNTs coating layer became more

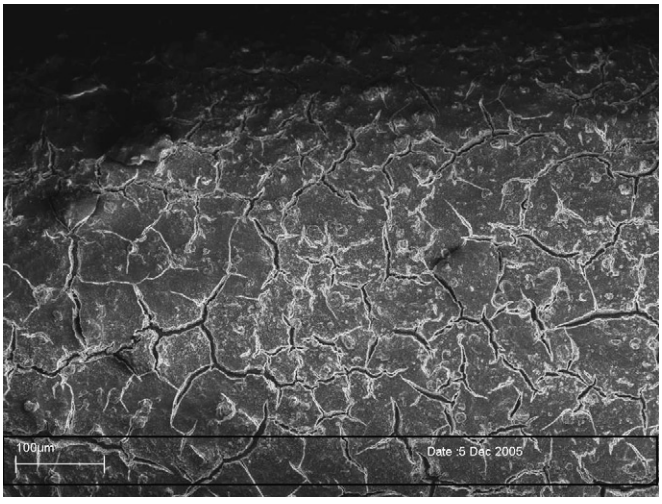

Fig. 4. FEG SEM image of HA plus CNTs coated Ti–6Al–4V alloy after sintering at 600 °C for 2 h under flowing nitrogen indicating the presence of surface cracks (but no peeling from the surface due to presence of CNTs that act as reinforcement fibres within the coating layer) when the deposit thickness is increased from 25 to 40 μm by increasing deposition time from 4 to 10 min.

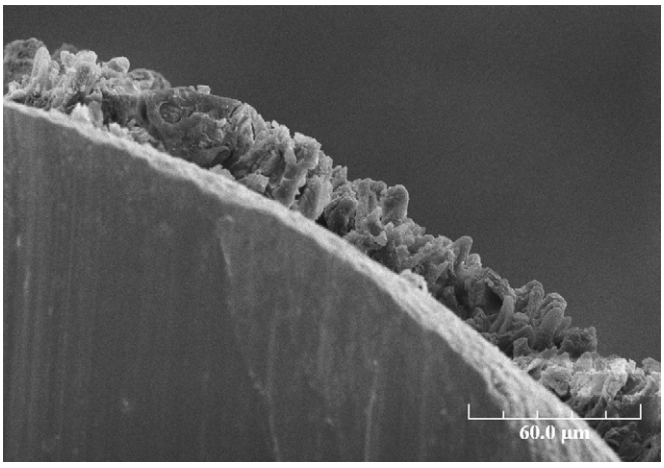

Fig. 5. FEG SEM image of EPD-formed HA plus CNTs coating layer obtained using a deposition voltage of 20 V dc and a deposition time of 4 min.

visible and effective leading to excessive strain within the coating layer. Currently further experiments are being conducted to optimise the relationships between processing parameters and quality of coating layers to prevent crack formation. Furthermore, thin coating layers (<10 μm) will be deposited to minimize crack formation due to thermal expansion mismatch between substrate and coating layers. Fig. 5 shows a FEG SEM image of EPD-coated HA plus 1 wt.% CNTs coating layer with a thickness of 25 μm using a deposition time of 4 min and an applied voltage of 20 V dc.

The effect of CNTs additions on the mechanical properties of the EPD-formed coating layers were also examined using nano-indentation and inter-laminar shear strength tests on samples sintered at 600 °C for 2 h under flowing nitrogen gas and the results were presented in Table 1. Monolithic HA coating has elastic modulus (E) and hardness (H) values of 15 and 4.88 GPa, respectively, whilst HA coatings reinforced with 2 wt.% CNTs have much increased E and H values of 178 and 36.44 GPa, respectively. It is seen in Table 1 that E and H values of HA layers increase with increasing amount of CNTs. When metallic alloys are used for biomedical applications, such as total hip replacement, the bonding strength (or inter-laminar shear strength) between implant and coating layer is the most important issue for life cycle of the replaced implant. For the inter-laminar shear tests, two plates of Ti–6Al–4V alloys (5 cm × 2 cm × 0.5 cm) were EPD-coated and then sintered together. Final bonded samples were subjected to tensile test and the strength of the coating layers was recorded as bonding or inter-laminar shear strength. As shown in Table 1, as the amount of CNTs increases within HA coating layer, the inter-laminar shear strength also increases significantly. Monolithic HA, HA plus 1 wt.% CNTs and HA plus 2 wt.% CNTs layers provided inter-laminar shear strength values of 0.7, 1.84 and 2.76 MPa, respectively, as shown in Table 1. Optimisation studies are now being conducted to obtain maximum inter-laminar shear strength by the addition of CNTs and using different EPD parameters without causing any crack formation within the coating layers.

Table 1
The effects of CNTs on the physical and mechanical properties of EPD-formed coating layers after sintering at 600 °C for 2 h under flowing nitrogen gas

Coating structure	Elastic modulus, E (GPa)	Hardness (GPa)	Inter-laminar shear strength (MPa)
HA	15 ± 0.4	4.88 ± 0.2	0.7 ± 0.04
HA + 1 wt.% CNTs	139 ± 7	18.9 ± 1.2	1.84 ± 0.1
HA + 2 wt.% CNTs	178 ± 8.5	36.44 ± 2.3	2.76 ± 0.14

4. Conclusion

It was presented in this work that Ti–6Al–4V medical alloys can easily be coated with monolithic hydroxyapatite or CNTs-reinforced HA bioactive materials for biomedical applications, such as total hip replacement using electrophoretic deposition as cost-effective, rapid and novel technique. Under constant voltage condition (20 V dc), a deposit thickness of 25 μm is achieved using a deposition time of 4 min and a colloidal suspension with a solids loading of 5 wt.% and resultant EPD-formed layer contains no surface microcracks. Both hardness, elastic modulus and inter-laminar shear strength of monolithic HA are increased by the addition of CNTs. Using ultra-fine HA powders, EPD-formed deposits can be sintered at low temperatures as low as 600 °C for 2 h and these layers bond to the implant surface with adequate strength against peeling. CNTs addition also helps to prevent peeling of the coating layers by acting as reinforcement network within the deposit. Further experiments are being conducted to investigate the optimum conditions to obtain HA layers reinforced with CNTs and necessary heat treatment conditions for EPD-formed layers with nano-structured nature in order to control crystallinity, homogeneity and surface morphology.

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